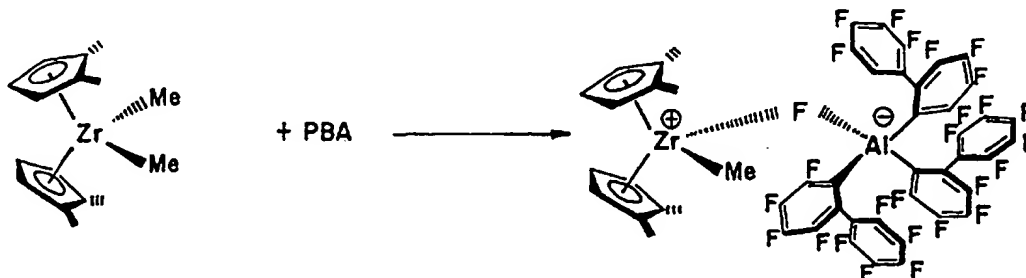




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(54) Title: USE OF GROUP 13 METAL PERFLUOROARYL FLUORO ANIONS IN METALLOCENE CATALYSTS FOR OLEFIN POLYMERIZATION



## (57) Abstract

A group 13 perfluoroaryl fluoro anion such as tris(2,2',2''-nonafluorobiphenyl)fluoroaluminate (PBA)- and its role as a cocatalyst in metallocene-mediated olefin polymerization is disclosed.

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## USE OF GROUP 13 METAL PERFLUOROARYL FLUORO ANIONS IN METALLOCENE CATALYSTS FOR OLEFIN POLYMERIZATION

This invention was made with Government support under Contract No. DE-FG02-86ER13511 awarded by the Department of Energy. The Government has certain rights in this invention.

This is a non-provisional application, from provisional application Serial No. 60/024,190, filed August 19, 1996.

### Background of the Invention

This invention relates to the compositions of matter useful as a catalyst system, to a method for preparing these catalyst systems and to a method for polymerization utilizing the catalyst system.

The use of soluble Ziegler-Natta type catalysts in the polymerization of olefins is well known in the prior art. In general, such systems include a Group IV-B metal compound and a metal or metalloid alkyl cocatalyst, such as aluminum alkyl cocatalyst. More broadly, it may be said to include a mixture of a Group I-III metal alkyl and a transition metal complex from Group IVB-VB metals, particularly titanium, zirconium, or hafnium with aluminum alkyl cocatalysts.

First generation cocatalyst systems for homogeneous metallocene Ziegler-Natta olefin polymerization, alkylaluminum chlorides ( $\text{AlR}_2\text{Cl}$ ), exhibit low ethylene polymerization activity levels and no propylene polymerization activity. Second generation cocatalyst systems, utilizing methyl aluminoxane (MAO), raise activities by several orders of magnitude. In practice however, a large stoichiometric excess of MAO over catalyst ranging from several hundred to ten thousand must be employed to have good activities and stereoselectivities. Moreover, it has not been possible to isolate characterizable metallocene active species using MAO. The third generation of cocatalyst,  $\text{B}(\text{C}_6\text{F}_5)_3$ , proves to be far more efficient while utilizing a 1:1 catalyst-cocatalyst ratio. Although active catalyst species generated with  $\text{B}(\text{C}_6\text{F}_5)_3$  are isolable and characterizable, the anion  $\text{MeB}(\text{C}_6\text{F}_5)_3^-$  formed after  $\text{Me}^-$  abstraction from metallocene dimethyl complexes is weakly coordinated to the electron-deficient metal center, thus resulting in a decrease of certain catalytic activities. The recently developed  $\text{B}(\text{C}_6\text{F}_5)_4^-$  type of non-coordinating anion exhibits some of the highest reported catalytic

activities, but such catalysts have proven difficult to obtain in the pure state due to poor thermal stability and poor crystallizability, which is crucial for long-lived catalysts and for understanding the role of true catalytic species in the catalysis for the future catalyst design. Synthetically, it also takes two more steps to prepare such an anion than for the neutral  
5 organo-Lewis acid.

### Summary of the Invention

Accordingly, it is an object of the subject invention to prepare and utilize a new class of olefin polymerization catalytic system.

10 A further object of the subject invention is a catalytic system which permits better control over molecular weight, molecular distribution, stereoselectivity, and comonomer incorporation.

Another object of the subject invention is a Ziegler-Natta type catalytic system which reduces the use of excess cocatalyst and activates previously unresponsive metallocenes.

15 These and other objects are attained by the subject invention whereby in one embodiment, a strong organo-Lewis acid, such as a (perfluoroaryl)aluminate anion and in particular tris(2,2',2'' nonafluorobiphenyl)fluoroaluminate (PBA<sup>-</sup>) is utilized as a highly efficient cocatalyst for metallocene-mediated olefin polymerization. PBA<sup>-</sup> exhibits higher catalytic activities and can activate previously unresponsive metallocenes. The synthesis of the  
20 stable perfluoroaryl aluminum anion, tris(2,2',2''-nonafluorobiphenyl)fluoroaluminate (PBA<sup>-</sup>) is accomplished with the use sterically encumbered perfluorobiphenyl ligand.

In one embodiment of the subject invention a strong organo-Lewis acid, such as a fluoraryl metal compound, is utilized to synthesize stoichiometrically precise, isolable/crystallographically characterizable, highly active "cation-like" metallocene  
25 polymerization catalysts.

In the subject application, "Cp" represents a cyclopentadienyl radical which may be substituted or unsubstituted, and:

(Cp)(Cp') or Cp-A-Cp' and Cp and Cp' are the same or different cyclopentadienyl ring substituted with zero to five substituent groups S and each substituent  
30 group S is, independently, a radical which can be hydrocarbyl, substituted-hydrocarbyl, halocarbyl, substituted-halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-

substituted organometalloid, or halogen radicals (the size of the radicals need not be limited to maintain catalytic activity; however, generally the radical will be a C<sub>1</sub> to C<sub>20</sub> radical) or Cp and Cp' are a cyclopentadienyl ring in which any two adjacent R groups are joined forming a C<sub>4</sub> to C<sub>20</sub> ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand such as indenyl, tetrahydroindenyl, fluorenyl, or octahydrofluorenyl and A is a bridging group which restricts rotation of the two Cp-groups.

Each carbon atom in the cyclopentadienyl radical ("Cp") may be, independently, unsubstituted or substituted with the same or different radical group which is a hydrocarbyl, substituted-hydrocarbyl, halocarbyl, substituted-halocarbyl hydrocarbyl radicals in which adjacent substituents are joined to form a ring of 4 to 10 or more carbon atoms, hydrocarbyl- and halocarbyl-substituted organometalloid radicals and halogen radicals.

More specifically, a fluoroaryl metal compound such as ZR'R''R'''F reacts with early transition metal or actinide alkyls to yield highly reactive cationic complexes:



where L, L' = cyclopentadienyl, cyclopentadienyl substituted or bridged cyclopentadienyl ligands such as CpACp', indenyl Cp, allyl Cp, benzyl Cp; substituted indenyl Cp; substituted allyl Cp; substituted benzyl Cp;  $\eta^5$ -1,2-Me<sub>2</sub> C<sub>5</sub>H<sub>3</sub>;  $\eta^5$ -1,3-(SiMe<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>;  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>; Me<sub>2</sub>Si( $\eta^5$ -Me<sub>4</sub>C<sub>5</sub>)(<sup>t</sup>BuN)

M = early transition metal or actinide, e.g., Ti, Zr, Hf, Th, U

R = PhCH<sub>2</sub>, alkyl or aryl group (C ≤ 20), hydride

R', R'', R''' = fluorinated phenyls, fluorinated biphenyl or fluorinated polycyclic fused ring groups

X = Al, Ga, In

15

As a specific example of the above, the reaction of PBA<sup>-</sup> with a variety of zirconocene dimethyl complexes proceeds rapidly and quantitatively to yield, after recrystallization from hydrocarbon solvents, in the catalytic complex set forth in Eq. 2.



Such catalytic complexes have been found to be active homogeneous catalysts for  $\alpha$ -olefin polymerization.

The cocatalyst of the subject invention may be referred to as  $\text{XR}'\text{R}''\text{R}'''\text{F}$ ; where  $\text{R}'$ ,  $\text{R}''$  and  $\text{R}'''$  represent at least one and maybe more fluorinated biphenyls or other fluorinated polycyclic groups, such as naphthyl. Two of the biphenyls may be substituted with a phenyl or other aryl group. Both the biphenyls and the phenyl groups should be highly fluorinated, preferably with only one or two hydrogens on a group, and most preferably, as in  $\text{PBA}^-$  with no hydrogens and all fluorines. X represents Al, Ga or In.

#### 10 Brief Description of the Drawings

The cocatalyst system of the subject invention can be better understood with reference to the drawings wherein:

Fig. 1 is a reaction pathway for the synthesis of  $\text{PBA}^-$ ;

Figs. 2a, 2b, 2c and 2d each show the reaction pathway for a catalyst system according to the subject invention.

#### Detailed Description of the Invention

Under a variety of reaction conditions and ratios of reagents, the reaction of 2-nonafluorobiphenyl lithium and  $\text{AlCl}_3$  all appear to lead to the formation of a compound with the structure  $\text{Ar}_3\text{FAlLi}^+$ , resulting from fluoride abstraction by the strongly Lewis acidic trisperfluoro-biphenyl aluminum species generated *in situ* (Fig. 1). Ion exchange metathesis of this lithium salt with  $\text{Ph}_3\text{CCl}$  results in the formation of stable trityl perfluorobiphenyl aluminate ( $\text{PBA}^-$ ). The structure of  $\text{PBA}^-$  has been characterized by X-ray diffraction and shows a non-associated trityl cation and aluminate anion.

#### 25 Isolation and Characterization of Cationic Group 4 Complexes Derived from PBA

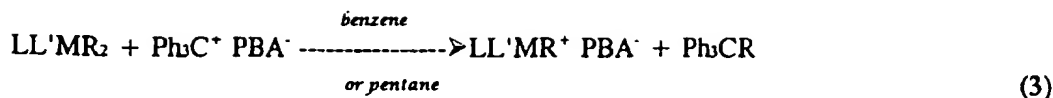
The reaction of  $\text{PBA}^-$  with various metallocene dialkyls readily generates the corresponding cationic complexes (Figs. 2a-2d). The  $\text{PBA}^-$  anion is weakly coordinated to the metal center via F bridges in these complexes. This coordination is evident from the large downfield shift ( $\geq 30$  ppm) of the Al-F F resonance in the  $^{19}\text{F}$  NMR as compared to that of free PBA. This coordination lowers the symmetry of the cation portion as well.

Furthermore, the coordinated anion is chiral. The relatively stable chirality of the anion stems from the bulkiness of the molecule which suppresses the rotation of perfluoroaryl rings and renders the geometry fixed, resulting in nine (9) sets of characteristic resonances in the  $^{19}\text{F}$  NMR. The influence of the anion chirality on the cation portion can be observed spectroscopically. In the reaction product of Fig. 2a, there are two diastereotopic  $\text{CH}_2\text{Ph}$  protons with  $^2J$  value of 11.4 Hz and two magnetically nonequivalent Cp rings, which reflects the chiral environment of the coordinated anion.

With diastereotopic ring substitution in the metallocene, the structure of the reaction product shown in Fig. 2b offers unique NMR probes for a better understanding of the molecular structure. Coordination of an achiral anion such as  $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$  to the metal center of the cation portion of Fig. 2b results in the observation of two diastereotopic Cp methyls and three types of Cp ring protons having different chemical shifts. However, in the reaction product of Fig. 2b with a coordinated chiral anion, all the Cp methyls (four types) and Cp ring protons (six types) have different chemical shifts, clearly indicating the chiral induction of the anion.

Constrained geometry catalysts (Figs. 2c and 2d) activated by PBA exhibit two distinct silyl methyls and four different Cp methyls. The structure of the reaction product of Fig. 3c has been characterized by X-ray diffraction and reveals a *chiral* PBA $^-$  anion coordinated via an F-bridge with Zr-F and Al-F bond lengths of (2.123) and (6) Å, respectively. The Zr-CH $_3$  bond distance of 2.21(1) Å is almost identical to that in  $\text{CGCZrMeMeB}(\text{C}_6\text{F}_5)_3$  (2.224 (5)) Å, reflecting the cationic character of the zirconium center. In cases where the bulkiness of cationic portion is increased, thereby pushing the anion away from the coordinative periphery, the product formed from the reaction appears neither stable nor isolable, *e.g.*,  $[(\text{C}_5\text{Me}_5)_2\text{ZrMe}_2]^+ \text{PBA}^-$ . However, this distant contact cation-anion pair exhibits extremely high activity for olefin polymerization when generated *in situ*.

$\text{Ph}_3\text{C}^+\text{PBA}^-$  has been synthesized in essentially quantitative yields as compared to the 30-50% yields experienced with  $\text{B}(\text{C}_6\text{F}_5)_3$ , currently a very important Lewis acidic cocatalyst in the polyolefin industry. More particularly, reaction of PBA $^-$  with group 4 methyls proceeds cleanly to yield cationic complexes such as set forth below.



5 L, L' = Cp<sup>+</sup> = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>

L, L' = Cp<sup>+</sup> = η<sup>5</sup>-1,2-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>

M = Ti, Zr, Hf

R = PhCH<sub>2</sub>, CH<sub>3</sub>, alkyl or aryl group with C ≤ 20; hydride

LL'MR<sup>+</sup> PBA<sup>-</sup> may be any cyclopentadienyl, substituted cyclopentadienyl or bridged  
 10 cyclopentadienyl complex paired with PBA<sup>-</sup>, such as Cp<sub>2</sub>ZrCH<sub>2</sub>Ph<sup>+</sup> PBA<sup>-</sup>; Cp<sub>2</sub>ZrH<sub>3</sub>PBA<sup>-</sup>;  
 Cp<sup>+</sup>ZrCH<sub>3</sub><sup>+</sup>-PBA<sup>-</sup>; (Cp<sup>TM5</sup>)<sub>2</sub>ZrCH<sub>3</sub><sup>+</sup>PBA<sup>-</sup>; Cp<sup>+</sup><sub>2</sub>ZrCH<sub>3</sub><sup>+</sup>PBA<sup>-</sup>; CGCZrCH<sub>3</sub><sup>+</sup> PBA<sup>-</sup>;  
 CGCTiCH<sub>3</sub><sup>+</sup> PBA<sup>-</sup>; and *rac*-Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrCH<sub>3</sub><sup>+</sup> PBA<sup>-</sup> (CGC = Me<sub>2</sub>Si(η<sup>5</sup>-Me<sub>4</sub>C<sub>5</sub>) BuN); (Ind  
 = η<sup>5</sup>-C<sub>9</sub>H<sub>6</sub>), 2-methyl (Ind) ZrCH<sub>3</sub><sup>+</sup> PBA<sup>-</sup>; (CpZrCp'Zr)<sub>2</sub> ZrCH<sub>3</sub><sup>+</sup>PBA<sup>-</sup>.

For polymerization of olefin monomers, catalytic activities of the cations generated  
 15 from PBA<sup>-</sup> can be greater than those of monomeric cations generated from B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in cases of  
 bulky L and L' ligands presumably because PBA<sup>-</sup> functions as a non-coordinating anion as  
 compared to the weakly coordinating anion MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. Polymerization reactions show very  
 high activities for α-olefin polymerization, and identify PBA<sup>-</sup> to be a truly non-coordinating  
 anion. When polymerizing α-olefins larger than ethylene and particularly propylene and  
 20 styrene, high isotacticity can be observed.

### Experimental

**Materials and Methods.** All manipulations of air-sensitive materials were performed with  
 rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual-  
 25 manifold Schlenk line or interfaced to a high-vacuum line (10<sup>-6</sup> Torr), or in a nitrogen-filled  
 vacuum atmospheres glovebox with a high capacity recirculator (1-2 ppm O<sub>2</sub>). Argon  
 (Matheson, prepurified) and ethylene (Matheson, polymerization grade) were purified by  
 passage through a supported MnO oxygen-removal column and an activated Davison 4A  
 molecular sieve column. Ether solvents were purified by distillation from Na/K  
 30 alloy/benzophenone ketyl. Hydrocarbon solvents (toluene, pentane) were distilled under  
 nitrogen from Na/K alloy. All solvents for vacuum line manipulations were stored *in vacuo*  
 over Na/K alloy in Teflon-valved bulbs. Deuterated solvents were obtained from Cambridge



Isotope Laboratories (all  $\geq 99$  atom %D) and were freeze-pump-thaw degassed and dried over Na/K alloy and stored in resealable flasks. Non-halogenated solvents were dried over Na/K alloy and halogenated solvents were distilled over  $P_2O_5$  and stored over activated Davison 4Å molecular sieves.  $BrC_6F_5$  (Aldrich) was vacuum distilled over  $P_2O_5$ .  $AlCl_3$ ,  $Ph_3CCl$  and  $n-BuLi$  (1.6M in hexanes) were purchased from Aldrich. The zirconocene and titanocene complexes  $Cp_2ZrMe_2$ ;  $Cp_2Zr(CH_2Ph)_2$ ;  $(1,2-Me_2C_5H_3)_2ZrMe_2$ ;  $[1,3-(SiMe_3)_2C_5H_3]_2ZrMe_2$ ;  $(C_5Me_5)_2ZrMe_2$ ,  $Me_2Si(Me_4C_5)(BuN)ZrMe_2$  and  $Me_2Si(Me_4C_5)BuNTiMe_2$  were prepared according to known procedures.

**Physical and Analytical Measurements.** NMR spectra were recorded on either Varian VXR 300 (FT 300 MHz,  $^1H$ ; 75 MHz,  $^{13}C$ ) or Varian Gemini-300 (FT 300 MHz,  $^1H$ ; 75 MHz,  $^{13}C$ ; 282 MHz,  $^{19}F$ ) instruments. Chemical shifts for  $^1H$  and  $^{13}C$  spectra were referenced using internal solvent resonances and are reported relative to tetramethylsilane.  $^{19}F$  NMR spectra were referenced to external  $CFCl_3$ . NMR experiments on air-sensitive samples were conducted in Teflon valve-sealed sample tubes (J. Young). Melting temperatures of polymers were measured by DSC (DSC 2920, TA Instruments, Inc.) from the second scan with a heating rate of 20°C/min.

### EXAMPLE 1

**Trityl Perfluorobiphenyl Aluminate,  $Ph_3C^+ PBA^-$ .** *n*-Butyllithium (1.6 M in hexanes, 25 mL, 40 mmol) was added dropwise to bromopentafluorobenzene (18.0 g, 9.1 mL, 72.9 mmol) in 100 mL of diethyl ether cooled by a cold-water bath. The mixture was then stirred for a further 12 h at room temperature. Removal of the solvent followed by vacuum sublimation at 60-65°C/10<sup>-4</sup> Torr gave 12.0 g of 2-bromononafluorobiphenyl as a white crystalline solid. Yield: 83.3%.  $^{19}F$  NMR ( $C_6D_6$ , 23°C):  $\delta$  -126.77 (d,  $^3J_{F-F} = 25.4$  Hz, 1 F, F-3), -135.13 (d,  $^3J_{F-F} = 18.9$  Hz, 1 F, F-6), -138.85 (d,  $^3J_{F-F} = 17.2$  Hz, 2 F, F-2'/F-6'), -148.74 (t,  $^3J_{F-F} = 20.8$  Hz, 1 F, F-4), -150.13 (t,  $^3J_{F-F} = 21.7$  Hz, 1 F, F-4'), -154.33 (t,  $^3J_{F-F} = 21.4$  Hz, 1 F, F-5), -160.75 (t,  $^3J_{F-F} = 23.9$  Hz, 2 F, F-3'/F-5').

To the above 2-bromononafluorobiphenyl (8.29 g, 21.0 mmol) in a mixed solvent of 70 mL of diethyl ether and 70 mL of pentane was gradually added 13.2 mL of *n*-butyllithium (1.6 M in hexanes, 21.0 mmol) at -78°C. The mixture was stirred for an

additional 2 h, and aluminum trichloride (0.67 g, 5.0 mmol) was then quickly added. The mixture was stirred at -78°C for 1 h and the temperature was then allowed to slowly rise to room temperature. A white suspension resulted after stirring for an additional 12 h. The mixture was filtered and the solvent removed from the filtrate *in vacuo*. To the yellow sticky residue was added 100 mL of pentane and the mixture was stirred for 1 h. The resulting white solid was collected by filtration and dried *in vacuo* to give 3.88 g of  $\text{Ar}^{\text{F}}_3\text{FAI}^+\text{Li}^+\text{OEt}$ : yield: 72.4%  $^1\text{H}$  NMR ( $\text{C}_7\text{D}_8$ , 23°C):  $\delta$  2.84 (q,  $J = 7.2$  Hz, 4 H, 2- $\text{CH}_2\text{O}$ ), 0.62 (t,  $J = 7.2$  Hz, 6 H, 2 $\text{CH}_3\text{CH}_2\text{O}$ -).  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ , 23°C):  $\delta$  -122.80 (s, br, 3 F, F-3), -134.86 (s, 3 F, F-6), -139.12 (s, 6 F, F-2'/F-6'), -153.95 (t,  $^3J_{\text{F-F}} = 18.3$  Hz, 3 F, F-4), -154.52 (t,  $^3J_{\text{F-F}} = 20.2$  Hz, 6 F, F-4'/F-5), -162.95 (s, 6 F, F-3'/F-5'), -176.81 (s, br, 1 F, Al-F). The above lithium salt (1.74 g, 1.62 mmol) and  $\text{Ph}_3\text{CCl}$  (0.48 g, 1.72 mmol) was suspended in pentane and stirred overnight and the resulting orange solid was collected by filtration and washed with pentane. The crude product was then redissolved in  $\text{CH}_2\text{Cl}_2$  and filtered through Celite to remove  $\text{LiCl}$ , followed by pentane addition to precipitate the orange solid. Recrystallization from  $\text{CH}_2\text{Cl}_2$ /pentane at -78°C overnight gave 1.56 g orange crystals of the title compound. Yield: 70.5%. Analytical and spectroscopic data for PBA are as follows:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 23°C):  $\delta$  8.25 (t,  $J = 7.5$  Hz, 3 H, *p*-H, Ph), 7.86 (t,  $J = 7.5$  Hz, 6 H, *m*-H, Ph), 7.64 (dd,  $J = 8.4$  Hz,  $J = 1.2$  Hz, 6 H, *o*-H, Ph), 1.28 (m), 0.88 (t) (pentane residue).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 23°C):  $\delta$  -121.05 (s, 3 F, F-3), -139.81 (s, 3 F, F-6), -141.19 (s, 6 F, F-2'/F-6'), -156.93 (t,  $^3J_{\text{F-F}} = 18.3$  Hz, 6 F, F-4'/F-4'), -158.67 (s, 3 F, F-5), -165.32 (s, 6 F, F-3'/F-5'), -175.60 (s, br, 1 F, Al-F). *Anal.* Calcd for  $\text{C}_{60}\text{H}_{15}\text{AlF}_{28}\cdot\text{C}_3\text{H}_{12}$ : C, 57.12; H, 1.99. Found: C, 57.16; H, 1.43.

## EXAMPLE 2

**$\text{Cp}_2\text{Zr-CH}_2\text{Ph}^+(\text{PBA})^-(1)$ .**  $\text{Cp}_2\text{Zr}(\text{CH}_2\text{Ph})_2$  (0.081 g, 0.20 mmol) and  $\text{Ph}_3\text{C}^+\text{PBA}^-$  (0.261 g, 0.20 mmol) were charged in the glove box into a 25-mL reaction flask with a filter frit and the flask was reattached to the high vacuum line. Toluene (15 mL) was then vacuum-transferred into this flask at -78°C. The mixture was slowly allowed to warm to room temperature and stirred for 4 h. The volume of toluene was next reduced to 5 mL and 10 mL of pentane was condensed into the flask at -78°C. A suspension which formed was quickly filtered and the orange crystalline solid which collected was dried under vacuum overnight. Yield, 0.22 g

(84.4%). Large orange crystals were obtained by slow cooling a pentane solution of the compound to -20°C over a period of several days. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 23°C): δ 6.95 (t, *J* = 7.8 Hz, 2 H, *m*-H, Ph), 6.80 (t, *J* = 7.5 Hz, 1 H, *p*-H, Ph), 6.46 (d, *J* = 7.2 Hz, 2 H, *o*-H, Ph), 5.45 (s, 5 H, Cp), 5.42 (s, 5 H, Cp), 2.47 (d, *J* = 11.4 Hz, 1 H, -CH<sub>2</sub>), 1.92 (d, *J* = 11.4 Hz, 1 H, -CH<sub>2</sub>). <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>, 23°C): δ -117.09 (t, <sup>3</sup>*J*<sub>F-F</sub> = 20.5 Hz, 3 F), -133.17 (t, <sup>3</sup>*J*<sub>F-F</sub> = 15.2 Hz, 3 F), -138.60 (d, <sup>3</sup>*J*<sub>F-F</sub> = 27.3 Hz, 3 F), -139.53 (t, <sup>3</sup>*J*<sub>F-F</sub> = 21.2 Hz, 3 F), -146.34 (s, br, 1 F, Al-F), -152.01 (t, <sup>3</sup>*J*<sub>F-F</sub> = 24.3 Hz, 3 F), -153.15 (t, <sup>3</sup>*J*<sub>F-F</sub> = 20.9 Hz, 3 F), -153.92 (t, <sup>3</sup>*J*<sub>F-F</sub> = 18.3 Hz, 3 F), -160.82 (d, <sup>3</sup>*J*<sub>F-F</sub> = 21.4 Hz, 3 F), -162.52 (t, <sup>3</sup>*J*<sub>F-F</sub> = 24.53 Hz, 3 F), <sup>13</sup>C NMR (C<sub>7</sub>D<sub>8</sub>, 23°C): δ 129.20 (d, <sup>3</sup>*J*<sub>CH</sub> = 156.2 Hz, Ph), 128.26 (d, <sup>3</sup>*J*<sub>CH</sub> = 157.1 Hz, Ph), 127.52 (s, ipso-Ph), 125.42 (d, <sup>3</sup>*J*<sub>CH</sub> = 158.1 Hz, Ph), 114.77 (d, <sup>3</sup>*J*<sub>CH</sub> = 176.5 Hz, Cp), 66.68 (t, <sup>3</sup>*J*<sub>CH</sub> = 122.8 Hz, -CH<sub>2</sub>), *Anal.* Calcd for C<sub>53</sub>H<sub>17</sub>AlF<sub>28</sub>Zr: C, 48.82; H, 1.31. Found: C, 48.77; H, 1.36.

### 15 EXAMPLE 3

#### Cp<sup>+</sup><sub>2</sub>ZrMe<sup>+</sup>PBA<sup>-</sup> (2).

The procedure is the same as that of synthesis of Example 1 above. Yield: 81.7%. <sup>1</sup>H NMR (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 23°C): δ 5.95 (s, br, 1 H, C<sub>5</sub>H<sub>3</sub>Me<sub>2</sub>), 5.77 (s, br, 1 H, C<sub>5</sub>H<sub>3</sub>Me<sub>2</sub>), 5.72 (s, br, 1 H, (C<sub>5</sub>H<sub>3</sub>Me<sub>2</sub>), 5.46 (s, br, 1 H, C<sub>5</sub>H<sub>3</sub>Me<sub>2</sub>), 5.70 (s, br, 1 H, C<sub>5</sub>H<sub>3</sub>Me<sub>2</sub>), 5.40 (s, br, 1 H, C<sub>5</sub>H<sub>3</sub>Me<sub>2</sub>), 2.11 (s, 3 H, C<sub>5</sub>H<sub>3</sub>Me<sub>2</sub>), 1.98 (s, 3 H, C<sub>5</sub>H<sub>3</sub>Me<sub>2</sub>), 1.76 (s, 3 H, C<sub>5</sub>H<sub>3</sub>Me<sub>2</sub>), 1.70 (s, 3 H, C<sub>5</sub>H<sub>3</sub>Me<sub>2</sub>), 0.28 (d, <sup>1</sup>*J*<sub>CH</sub> = 120.3 Hz, Zr-<sup>13</sup>CH<sub>3</sub>). <sup>19</sup>F NMR (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 23°C) is similar to the product of Example 1 except for a different chemical shift for the bridging F at -143.38 ppm. *Anal.* Calcd for C<sub>51</sub>H<sub>21</sub>AlF<sub>28</sub>Zr: C, 47.71; H, 1.65. Found: 47.46; H, 1.37.

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### EXAMPLE 4

#### (Cp<sup>TMS</sup>)<sub>2</sub>ZrMe<sup>+</sup>PBA<sup>-</sup> (3) .

This complex was prepared as described in Example 1 above. It decomposes in toluene solution within 2 h at 25°C and undergoes rapid decomposition to a myriad of unidentified products at higher temperatures. Characterization of the complex is based on very clean NMR scale reactions. This complex was generated *in situ* for polymerization studies. <sup>1</sup>H NMR

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$C_7D_8$ , 23°C):  $\delta$  6.88 (s, br, 1 H,  $C_5H_5TMS_2$ ), 6.71 (t,  $J = 2.1$  Hz, 1 H,  $C_5H_5TMS_2$ ), 6.31 (s, br, 1 H,  $C_5H_5TMS_2$ ), 6.23 (s, br, 1 H,  $C_5H_5TMS_2$ ), 5.79 (s, br, 1 H,  $C_5H_5TMS_2$ ), 5.71 (s, br, 1 H,  $C_5H_5TMS_2$ ), 0.70 (s, br, 3 H, Zr-CH<sub>3</sub>), 0.17 (s, 3 H,  $C_5H_5TMS_2$ ), 0.10 (s, 3 H,  $C_5H_5TMS_2$ ), -0.05 (s, 3 H,  $C_5H_5TMS_2$ ), -0.07 (s, 3 H,  $C_5H_5TMS_2$ ).  $^{19}F$  NMR ( $C_7D_8$ , 23°C):  
 5  $\delta$  -112.12 (d,  $^3J_{F-F} = 12.2$  Hz, 3 F), -133.22 (t,  $^3J_{F-F} = 15.5$  Hz, 3 F), -137.49 (s, 3 F), -138.40 (t,  $^3J_{F-F} = 21.7$  Hz, 3 F), -144.23 (s, br, 1 F, Al-F), -153.41 (m, 6 F), -154.15 (t,  $^3J_{F-F} = 21.2$  Hz, 3 F), -161.80 (d,  $^3J_{F-F} = 18.3$  Hz, 3 F), -162.82 (t,  $^3J_{F-F} = 21.4$  Hz, 3 F).

#### 10 EXAMPLE 5

(Cp'<sup>+</sup><sub>2</sub>ZrMe<sup>+</sup>(PBA)<sup>-</sup> (4) is too thermally unstable at 25°C to isolate. The  $^1H$  NMR monitored reaction of Cp'<sup>+</sup><sub>2</sub>ZrMe<sub>2</sub> and Ph<sub>3</sub>C<sup>+</sup>PBA<sup>-</sup> in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> clearly reveals the formation of Ph<sub>3</sub>CCH<sub>3</sub> ( $\delta$  2.15) and a broad singlet at  $\delta$  0.25 assignable to the ZrCH<sub>3</sub><sup>+</sup> group. More than 4 Cp methyl resonances at  $\delta$  1.97-1.72 ppm with different intensities are observed indicating the  
 15 decomposition. Complex 4 was generated *in situ* for polymerization studies.  $^{19}F$  NMR (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>):  $\delta$  -114.77 (s, br, 3 F), -132.11 (t,  $^3J_{F-F} = 15.2$  Hz, 3 F), -136.84 (t,  $^3J_{F-F} = 22.0$  Hz, 3 F), -137.29 (s, br, 3 F), -150.90 (t,  $^3J_{F-F} = 20.9$  Hz, 3 F), -151.85 (t,  $^3J_{F-F} = 23.9$  Hz, 3 F), -152.47 (t,  $^3J_{F-F} = 24.5$  Hz, 3 F), -155.78 (s, br, 1 F Al-F), -160.02 (d,  $^3J_{F-F} = 16.5$  Hz, 3 F), -161.06 (t,  $^3J_{F-F} = 21.2$  Hz, 3 F).

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#### EXAMPLE 6

Me<sub>2</sub>Si(<sup>t</sup>BuN)(C<sub>5</sub>Me<sub>4</sub>)ZrMe<sup>+</sup>PBA<sup>-</sup>.

Me<sub>2</sub>Si(Me<sub>4</sub>C<sub>5</sub>)(<sup>t</sup>BuN) ZrMe<sub>2</sub> (0.148 g, 0.4 mmol) and Ph<sub>3</sub>C<sup>+</sup> PBA<sup>-</sup> (0.523, 0.4 mmol) were reacted in the same manner as in Example 1 to yield 0.35 g of the above complex as a white  
 25 crystalline solid. Yield: 64.8%. The complex is quite soluble in pentane and cold pentane was used to wash the product.  $^1H$  NMR ( $C_7D_8$ , 23°C):  $\delta$  1.98 (s, 3 H, C<sub>5</sub>Me<sub>4</sub>), 1.82 (s, 3 H, C<sub>5</sub>Me<sub>4</sub>), 1.76 (s, 3 H, C<sub>5</sub>Me<sub>4</sub>), 1.27 (s, 3 H, C<sub>5</sub>Me<sub>4</sub>), 0.93 (s, 9 H, N-<sup>t</sup>Bu), 0.24 (s, 3 H, SiMe<sub>2</sub>), 0.18 (s, 3 H, Zr-CH<sub>3</sub>), 0.15 (s, 3 H, SiMe<sub>2</sub>),  $^{19}F$  NMR ( $C_7D_8$ , 23°C)  $\delta$  -108.92 (s, br, 1 F, Al-F), -117.26 (s, br, 3 F), -133.19 (t,  $^3J_{F-F} = 12.1$  Hz, 3 F), -139.25 (s, 6 F), -152.53  
 30 (t,  $J_{F-F} = 21.2$  Hz, 3 F), -153.00 (d,  $^3J_{F-F} = 21.2$  Hz, 3 F), -153.00 (d,  $^3J_{F-F} = 21.4$  Hz, 3 F),

-153.76 (t,  $^3J_{\text{F-F}} = 24.3$  Hz, 3 F), -160.94 (t,  $^3J_{\text{F-F}} = 22.6$  Hz, 3 F), -162.80 (t,  $^3J_{\text{F-F}} = 21.4$  Hz, 3 F).  $^{13}\text{C}$  NMR ( $\text{C}_7\text{D}_8$ , 23°C):  $\delta$  130.19 ( $\text{C}_5\text{Me}_4$ ), 129.09 ( $\text{C}_5\text{Me}_4$ ), 127.18 ( $\text{C}_5\text{Me}_4$ ), 126.44 ( $\text{C}_5\text{Me}_4$ ), 124.33 ( $\text{C}_5\text{Me}_4$ ), 56.63 (N-CMe<sub>3</sub>), 38.58 (q,  $J = 120.6$  Hz, N-CMe<sub>3</sub>), 32.70 (q,  $J = 120.8$  Hz, Zr-CH<sub>3</sub>), 15.75 (q,  $J = 127.9$  Hz,  $\text{C}_5\text{Me}_4$ ), 14.05 (q,  $J = 128.0$  Hz,  $\text{C}_5\text{Me}_4$ ), 12.00 (q,  $J = 127.8$  Hz,  $\text{C}_5\text{Me}_4$ ), 10.18 (q,  $J = 128.1$  Hz,  $\text{C}_5\text{Me}_4$ ), 8.49 (q,  $J = 121.0$  Hz, SiMe<sub>2</sub>), 6.52 (q,  $J = 120.9$  Hz, SiMe<sub>2</sub>). *Anal.* Calcd for  $\text{C}_{52}\text{H}_{30}\text{AlF}_{28}\text{NSiZr}$ : C, 46.37; H, 2.25; N, 1.04. Found: C, 46.65; H, 2.13; N, 0.89.

#### EXAMPLE 7

##### 10 $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(t\text{BuN})\text{TiMe}^+\text{PBA}^-$ .

$\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(t\text{BuN})\text{TiMe}_2$  (0.065 g, 0.2 mmol) and  $\text{Ph}_3\text{C}^+\text{PBA}^-$  (0.261, 0.2 mmol) were reacted in the same manner as in Example 1 to yield 0.12 g of the above complex as a yellow crystalline solid. Yield: 46.0%. Due to its good solubility in pentane, a significant amount of the product remained in the filtrate, resulting in a low isolated yield. An NMR scale reaction indicates the formation of the compound in quantitative yield when the isolation is not required.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 23°C):  $\delta$  2.01 (s, 3 H,  $\text{C}_5\text{Me}_4$ ), 1.72 (s, 3 H,  $\text{C}_5\text{Me}_4$ ), 1.61 (s, 3 H,  $\text{C}_5\text{Me}_4$ ), 1.20 (s, 3 H,  $\text{C}_5\text{Me}_4$ ), 0.93 (s, 9 H, N-*t*Bu), 0.75 (d,  $J = 3.9$  Hz, 3 H), 0.21 (s, H), 0.06 (s, 3 H).  $^{19}\text{F}$  NMR is similar to that of 3 except slightly different chemical shifts. *Anal.* Calcd for  $\text{C}_{52}\text{H}_{30}\text{AlF}_{28}\text{NSiTl}$ : C, 47.91; H, 2.32; N, 1.07. Found: C, 47.47; H, 1.96; N, 0.87.

#### EXAMPLE 8

**Synthesis of  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}^+\text{PBA}^-$ .**  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}_2$  (0.082 g, 0.20 mmol) and  $\text{Ph}_3\text{C}^+\text{PBA}^-$  (0.261, 0.20 mmol) were reacted in the same manner as for the synthesis of 1 above to yield 0.19 g of the title complex as an orange crystalline solid. Yield: 68.6%. Two diastereomers are found in a 1.3:1 ratio.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 23°C) for diastereomer A (56%):  $\delta$  7.45 (d,  $J = 8.7$  Hz, 1 H, C<sub>6</sub>-H), 7.27-6.88 (m, 4 H, C<sub>6</sub>-H), 6.67 (t,  $J = 7.5$  Hz, 2 H, C<sub>6</sub>-H), 5.88 (t,  $J = 7.5$  Hz, 1 H, C<sub>6</sub>-H), 6.82 (t,  $J = 3.3$  Hz, 1 H, C<sub>5</sub>- $\beta$  H), 5.96 (d,  $J = 3.3$  Hz, 1 H, C<sub>5</sub>- $\beta$  H), 5.69 (s, br, 1 H, C<sub>5</sub>- $\alpha$  H), 5.19 (d,  $J_{\text{HF}} = 2.1$  Hz, 3 H, Zr-CH<sub>3</sub>). Diastereomer B (44%):  $\delta$  7.94 (d,  $J = 8.7$  Hz, 1 H, C<sub>6</sub>-H), 7.27-6.88 (m, 4 H, C<sub>6</sub>-H), 6.58 (t,  $J = 7.5$  Hz, 2 H, C<sub>6</sub>-H), 5.79 (t,  $J = 7.5$  Hz, 1 H, C<sub>6</sub>-H), 6.42 (d,  $J = 3.3$  Hz, 1 H, C<sub>5</sub>-

$\beta$  H), 5.85 (d,  $J = 3.3$  Hz, 1 H, C $\beta$ -H), 5.56 (s, br, 1 H, C $\beta$ -H), 4.80 (d,  $J = 3.3$  Hz, 1 H, C $\beta$ -H), 0.46 (s, 3 H, SiMe $_2$ ), 0.25 (s, 3 H, SiMe $_2$ ), -0.64 (d,  $J_{HF} = 2.1$  Hz, 3 H, Zr-CH $_3$ ).  $^{19}\text{F}$  NMR (C $_6\text{D}_6$ , 23°C) for diastereomer A (56%):  $\delta$  -115.86 (s, br, 3 F), -132.23 (s, br, 1 F, Al-F), -133.76 (t,  $^3J_{F-F} = 18.3$  Hz, 3 F), -138.53 (s, br, 3 F), -139.40 (t,  $^3J_{F-F} = 18.3$  Hz, 3 F), -153.10 (t,  $^3J_{F-F} = 18.3$  Hz, 3 F), -153.44 (t,  $^3J_{F-F} = 18.3$  Hz, 3 F), -154.72 (t,  $^3J_{F-F} = 21.2$  Hz, 3 F), -161.18 (t,  $^3J_{F-F} = 18.3$  Hz, 3 F), -162.86 (t,  $^3J_{F-F} = 18.3$  Hz, 3 F). Diastereomer B (44%):  $\delta$  -113.48 (s, br, 3 F), -133.76 (t,  $^3J_{F-F} = 21.2$  Hz, 3 F), -134.44 (s, br, 1 F, Al-F), -137.89 (s, br, 3 F), -139.09 (t,  $^3J_{F-F} = 18.3$  Hz, 3 F), -153.10 (t,  $^3J_{F-F} = 18.3$  Hz, 3 F), -153.28 (t,  $^3J_{F-F} = 18.3$  Hz, 3 F), -153.73 (t,  $^3J_{F-F} = 18.3$  Hz, 3 F), -161.03 (t,  $^3J_{F-F} = 18.3$  Hz, 3 F), -162.68 (t,  $^3J_{F-F} = 18.3$  Hz, 3 F).  $^{13}\text{C}$  NMR (C $_6\text{D}_6$ , 23°C):  $\delta$  134.02, 132.96, 132.43, 128.31, 127.67, 127.28, 126.95, 126.64, 126.21, 125.90, 125.81, 124.88, 124.20, 124.10, 123.57, 122.89, 122.01, 121.98 (C $_6$ -ring), 119.16, 116.56, 115.96, 114.94, 112.90, 112.79 (C $_3$ -ring), 91.82, 90.95, 89.30, 89.20, (C $_3$ -Si), 51.46, 51.73, (Zr-CH $_3$ ), -1.31, -2.13, -2.88, -3.51 (SiMe $_2$ ). *Anal.* Calcd for C $_{57}\text{H}_{21}\text{AlF}_{28}\text{SiZr}$ : C, 49.47; H, 1.53. Found: C, 49.09; H, 1.27.

#### EXAMPLES 9-15

**Ethylene and Propylene Polymerization.** In a glove box, a 250 mL flamed, 3-necked round-bottom flask equipped with a magnetic stirring bar was charged with metallocene (5-10 mg) and cocatalyst Ph $_3\text{C}^+$  PBA $^-$  in a 1:1 molar ratio and the flask was then reattached to the high vacuum line. A measured amount of dry toluene (50 mL for this study) was next condensed onto the solids and the mixture was warmed to room temperature with stirring for 10 min to preactivate the catalyst. The resulting solution was then equilibrated at desired reaction temperature using an external constant temperature bath. Gaseous ethylene or propylene was next introduced with rapid stirring and the pressure was maintained at 1.0 atm by means of a mercury bubbler. After a measured time interval, the reaction was quenched by the addition of 2% acidified methanol. The polymer was collected by filtration, washed with methanol, and dried on high vacuum line overnight to a constant weight. Highly isotactic polypropylene is the result of propylene polymerization using PBA $^-$  as a catalyst. The reaction parameters and results are set forth in the Table.

**TABLE**  
**Ethylene Polymerization Activities with Metallocene/Ph<sub>3</sub>C<sup>+</sup> PBA<sup>-</sup> Catalysts and Polymer Properties**

Example No.	catalyst	T <sub>p</sub> (°C)	μmol of cat.	reaction time (min)	polymer yields (g)	activity <sup>a</sup> (g of polymer/(mol of cat atm h))	M <sub>w</sub> <sup>c</sup>	M <sub>w</sub> /M <sub>n</sub>	T <sub>m</sub> <sup>d</sup> (°C)	ΔH <sub>f</sub> (cal/g)
5.	Cp <sub>2</sub> ZrMe <sub>2</sub>	25	20	20	0	0				
6.	Cp <sup>+</sup> <sub>2</sub> ZrMe <sub>2</sub>	25	20	30	0.18	1.80 x 10 <sup>4</sup>	5.46 x 10 <sup>3</sup>	6.0	139.4	40.5
7.	(Cp <sup>TM5</sup> ) <sub>2</sub> ZrMe <sub>2</sub>	25	15	2.0	0.54	1.08 x 10 <sup>6</sup>	1.26 x 10 <sup>6</sup>	5.6	142.3	29.5
8.	Cp <sup>+</sup> <sub>2</sub> ZrMe <sub>2</sub>	25	15	0.67	1.15	6.90 x 10 <sup>6</sup>	8.97 x 10 <sup>4</sup>	4.6	138.0	53.9
9.	CGCZrMe <sub>2</sub>	25	15	10	0	0				
10.	CGCTiMe <sub>2</sub>	60	30	30	0.20	1.33 x 10 <sup>4</sup>	2.05 x 10 <sup>6</sup>	3.9	139.2	19.5
11.	CGCTiMe <sub>2</sub>	110	30	5.0	0.20	8.00 x 10 <sup>4</sup>	2.05 x 10 <sup>6</sup>	3.1	142.5	24.4
12. <sup>e</sup>	<i>rac</i> -Me <sub>2</sub> Si(Ind) <sub>2</sub> ZrMe <sup>+</sup> PBA <sup>-</sup>	60	20	120	0.65	1.63 x 10 <sup>4</sup>	2.34 x 10 <sup>4</sup>	3.59	145	-

a. Carried out at 1 atm of ethylene and 50 mL of toluene on high vacuum line

b. Reproducibility between runs = 10-15 %

c. GPC relative to polystyrene standards

d. DSC from the second scan

e. For propylene polymerization

The table summarizes ethylene polymerization activities by various metallocene catalysts activated with PBA<sup>-</sup>. Cp<sub>2</sub>ZrMe<sub>2</sub> exhibits virtually no activity for ethylene polymerization. This is presumably caused by the anion coordination through a Zr-F-Al bridge (Figure 2a). However, as the ligand framework of the cation portion changes from Cp (C<sub>5</sub>H<sub>5</sub>), to Cp<sup>''</sup>(1,2,-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>), to Cp<sup>TM5</sup><sub>2</sub> [1,3-(SiMe<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>], to Cp'(C<sub>5</sub>Me<sub>3</sub>), the activity for ethylene polymerization increases dramatically (Examples 1-4) and reaches the highest level of 6.90x10<sup>6</sup>g of PE/(mole of cat-atm-h) with the Cp'<sub>2</sub>ZrMe<sub>2</sub> catalyst (Example 4). The polyethylene produced is highly linear with melting temperature T<sub>m</sub> of 139.4°C and crystalline with heat of fusion ΔH<sub>μ</sub> of 53.9 cal/g. As the bulkiness of cation portion increases, the degree of anion coordination drops significantly, clearly reflecting the relationship between the polymerization activity and the relative tightness of cation-anion pairing structure.

In the case of the Cp' ligand, the separation of cation and anion reaches an optimum condition for reactivity that results in the maximum polymerization activity and instability of the cationic complex derived therefrom as well. Such a dramatic influence of the ligand framework substituents on polymerization activity is unprecedented and suggests the special features of the subject anion. PBA is apparently such a large anion that separation of anion and cation can be easily and substantially tuned and optimized by selecting the appropriate bulky cation.

For the sterically more accessible CGC type of catalyst, PBA<sup>-</sup> promotes no catalytic activity at room temperature, resulting from the strong anion coordination as reflected by the 66 ppm down-field shift of the Al-F F resonance as compared to PBA<sup>-</sup> (Figure 2c, Example 5). However, as the temperature of polymerization increases, the polymerization activity increases dramatically (Examples 5-7) presumably due to a higher degree of separation of cation-anion pairs at higher temperatures.

While the invention has been described with reference to a preferred embodiment, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that



the invention will include all embodiments and equivalents falling within the scope of the appended claims.

Various features of the invention are set forth in the following claims.

What is claimed is:

1. A catalytic complex of the structure:  $(LL' MR)^+ XR'R''R'''F$  where
  - $L, L'$  = a cyclopentadienyl ligand
  - $M$  = early transition metal or actinide
  - $R$  =  $PhCH_2$ , alkyl, benzyl or aryl group ( $C \leq 20$ ), hydride
  - $X$  = Al, Ga, In
  - $R', R'', R'''$  = fluorinated phenyl, fluorinated biphenyl or fluorinated polycyclic fused ring groups.
2. The complex of Claim 1 wherein  $M = Ti, Zr, Hf$ .
3. The complex of Claim 1 wherein said polycyclic fused ring groups include naphthyl, anthryl, and fluorenyl.
4. The method of Claim 1, wherein said cyclopentadienyl ligand is selected from the group consisting of indenyl, allyl, benzyl ( $C \leq 20$ ),  $\eta^5-C_5H_5$ ;  $\eta^5-1,2-Me_2 C_5H_3$ ;  $\eta^5-1,3-(SiMe_3)_2 C_5H_3$ ;  $\eta^5-C_5Me_5$  and  $Me_2Si(\eta^5-Me_4C_5)(tBuN)$ .
5. A method of preparing a catalyst system including the steps of adding a perfluoroaryl aluminate anion to a cationic metallocene.
6. The method of Claim 5, wherein said perfluoroaryl aluminate is tris (2,2',2''-nonafluorobiphenyl) fluoro aluminate.
7. The method of Claim 5, wherein said cationic metallocene is a cyclopentadienyl ligand.

8. The method of Claim 5, wherein said cationic metallocene ligands are selected from the group consisting of indenyl, allyl, benzyl,  $\eta^5\text{-C}_5\text{H}_5$ ;  $\eta^5\text{-1,2-Me}_2\text{C}_5\text{H}_3$ ;  $\eta^5\text{-1,3-(SiMe}_3)_2\text{C}_5\text{H}_3$ ;  $\eta^5\text{-C}_5\text{Me}_5$  and  $\text{Me}_2\text{Si}(\eta^5\text{-Me}_4\text{C}_5)(\text{tBuN})$ .

9. A method of polymerizing a monomer comprising the steps of adding the catalyst  $(\text{LL}'\text{MR})^+ \text{XR}'\text{R}''\text{R}'''\text{F}^-$  where

- L, L' = a cyclopentadienyl ligand  
 M = early transition metal or actinide  
 R =  $\text{PhCH}_2$ , alkyl, benzyl or aryl group ( $\text{C} \leq 20$ ), hydride  
 X = Al, Ga, In  
 R', R'', R''' = Fluorinated phenyl, fluorinated biphenyl or fluorinated polycyclic fused ring groups.

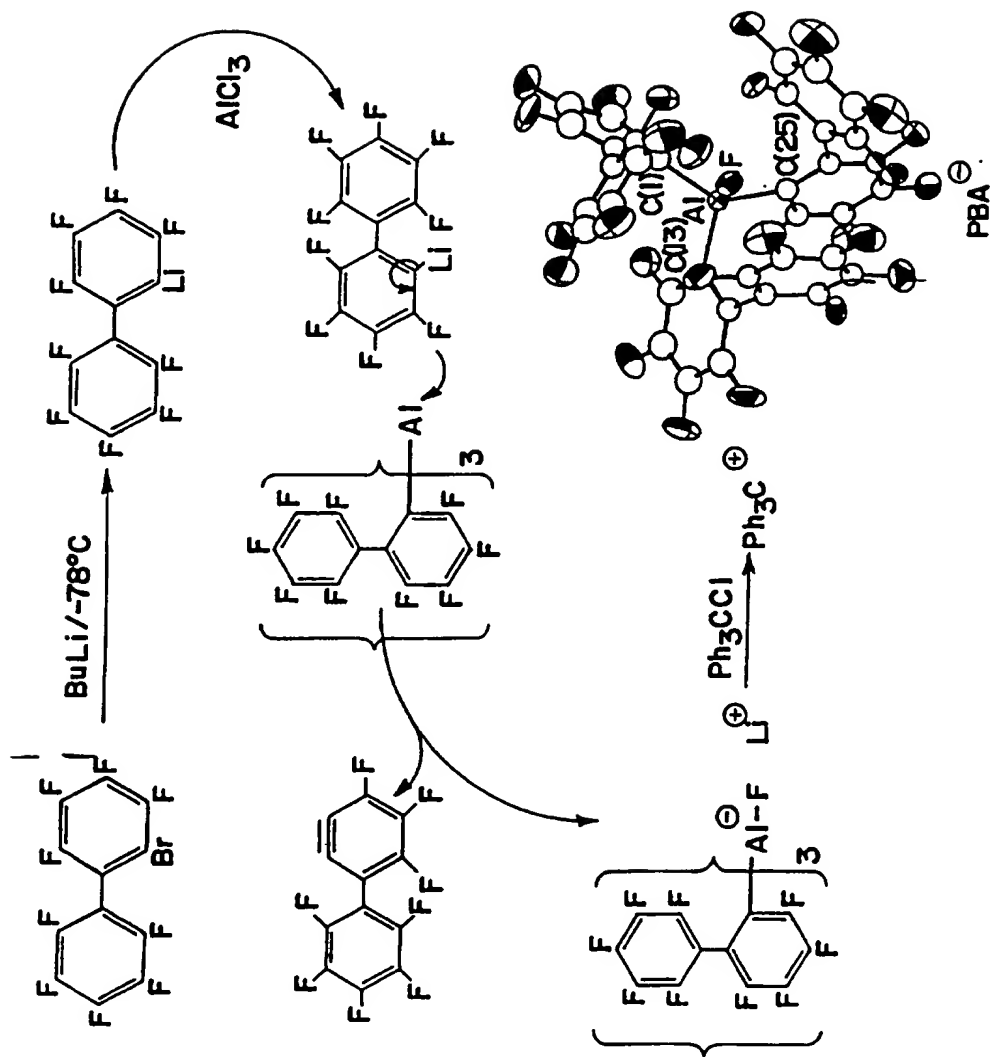
10. The method of Claim 7 wherein said reaction is carried out at ambient conditions.

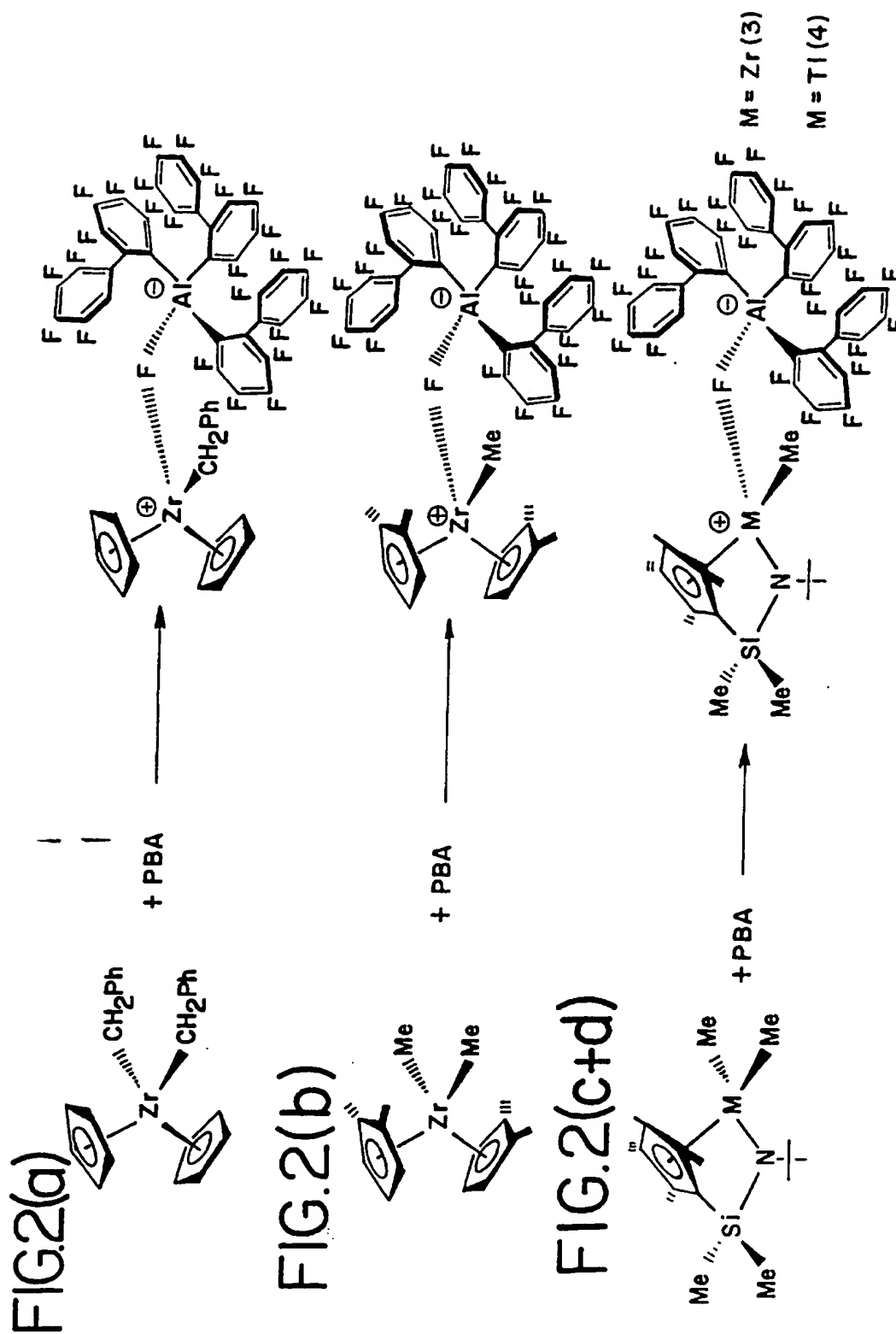
11. The method of Claim 9, wherein said reaction is initiated at temperatures from  $25^\circ\text{C}$  to  $110^\circ\text{C}$ .

12. The method of Claim 9, wherein said monomer is an  $\alpha$ -olefin.

13. The method of Claim 9, wherein said cyclopentadienyl ligand is selected from the group consisting of indenyl, allyl, benzyl ( $\text{C} \leq 20$ ),  $\eta^5\text{-C}_5\text{H}_5$ ;  $\eta^5\text{-1,2-Me}_2\text{C}_5\text{H}_3$ ;  $\eta^5\text{-1,3-(SiMe}_3)_2\text{C}_5\text{H}_3$ ;  $\eta^5\text{-C}_5\text{Me}_5$  and  $\text{Me}_2\text{Si}(\eta^5\text{-Me}_4\text{C}_5)(\text{tBuN})$ .

14. The method of Claim 9, wherein said monomer is selected from the group of ethylene, propylene and styrene.





## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/14523

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :Please See Extra Sheet

US CL :Please See Extra Sheet

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/102, 103, 117, 153; 526/127, 160, 943; 534/11, 15; 556/27, 28, 43, 53, 58, 187

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3,928,303 A (YASUI ET AL) 23 December 1975.	1-14
A	US 5,066,741 A (CAMPBELL, JR.) 19 November 1991.	1-14
A	US 5,391,661 A (NAGANUMA ET AL) 21 February 1995.	1-14
A,P	US 5,602,269 A (BIAGINI ET AL) 11 February 1997.	1-14
A	JORDAN, R.F. et al., Reactive Cationic Dicyclopentadienylzirconium(IV) Complexes, J. Am. Chem. Soc., 1986, vol. 108, pp. 1718-1719.	1-14

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*B* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

01 DECEMBER 1997

Date of mailing of the international search report

2.2 DEC 1997

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**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US97/14523

**A. CLASSIFICATION OF SUBJECT MATTER:**

IPC (6):

B01J 31/00, 37/00; C08F 4/02, 4/44, 4/60; C07F 5/00, 9/00, 17/00, 11/00, 5/06

**A. CLASSIFICATION OF SUBJECT MATTER:**

US CL :

502/102, 103, 117, 153; 526/127, 160, 943; 534/11, 15; 556/27, 28, 43, 53, 58, 187

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